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Design and Synthesis of CVD Precursors to Thin
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by

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DESIGN AND SYNTHESIS OF CVD PRECURSORS
TO THIN FILM CERAMIC MATERIALS

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ABSTRACT

The application of cyclic organometallic compounds as single source precursors for the chemical vapor deposition of materials such as AlN and SiC is discussed and new results relating to the decomposition of a novel SiC CVD precursor are presented. The decomposition of the cyclic carbosilane [μ -(CH₂)₂Si(CH₃)(H)Si(CH₃)-(CH₂SiH₂CH₃)], (I) on a heated glassy carbon substrate in an ultrahigh vacuum molecular beam system has been studied by pulsing the precursor molecule onto the surface and following the mass spectrum as a function of the substrate surface temperature. The evolution of CH₃SiH₂, C₂H₅ and CH₃ was evidenced, suggesting loss of excess carbon as C₁ and C₂ species.

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INTRODUCTION

Although organometallic compounds have been used for well over twenty years in the chemical vapor deposition of inorganic thin films [1], efforts to specifically design and synthesize such compounds for use in CVD have only recently received significant attention [2]. For most MOCVD processes each element required in the final inorganic film is supplied individually in the form of a relatively simple molecular source, such as trimethylgallium and arsine in the case of GaAs deposition. Since these deposition processes generally yield inorganic compounds containing two or more elemental components, at least two molecular sources are required, usually in combination with a carrier gas such as hydrogen. Problems associated with chemical interactions between the molecular sources, their differing thermolysis and chemisorption behavior, as well as the complex flow dynamics and mixing in the CVD reactors, limits the applicability and adds to the cost of CVD processing; moreover, control of the composition, homogeneity and microstructure of the product thin films is often difficult.

The availability of suitable single-source precursors for these CVD processes may help to overcome some of the current limitations of CVD processing. Finally, the thermal instability of the substrate or the underlying device structure often presents severe limitations on the film deposition methodology, driving the search for thermal CVD precursors which will work effectively at lower substrate temperatures.

This need for lower temperature, single-component precursors for CVD processes is particularly acute in the case of materials such

as aluminum nitride, silicon carbide and silicon nitride. The preparation of dense, uniform, and stoichiometric thin films of these highly refractory materials at temperatures less than 1000 °C has proven to be an especially challenging problem for thermal CVD processing [1].

We have been exploring the use of designed organometallic precursors for the CVD of these materials and have initiated studies of various cyclic compounds as potential precursors. In the case of AlN, our attention has focussed on the use of dimethylaluminum amide, $[(CH_3)_2AlNH_2]_3$, a molecular compound whose structure contains six-membered $(AlN)_3$ rings, much like the $(AlN)_3$ rings which make up the wurzite structure of AlN [3]. This compound was used successfully to obtain dense, stoichiometric, polycrystalline AlN films at temperatures as low as 500 °C [4].

In the case of SiC our initial studies have centered on a cyclic carbosilane, $[\mu-(CH_2)_2Si(CH_3)(H)Si(CH_3)(CH_2SiH_2CH_3)]$, (I) in which the built-in strain energy associated with the 4-membered $(SiC)_2$ ring apparently leads to a relatively facile thermal decomposition, enabling the preparation of stoichiometric SiC films at a substantially lower deposition temperature than had been demonstrated previously for thermal CVD of this material [5]. We report here the results of recent studies on the adsorption and thermal decomposition of this precursor on a heated glassy carbon substrate.

EXPERIMENTAL SECTION

The decomposition kinetics of the silicon carbide precursor and the formation of silicon carbide films were carried out in the ultrahigh vacuum molecular beam system. The salient features of this system include the following: a main vacuum chamber, in which silicon or glassy carbon samples were mounted on a manipulator in line with the system axis for study; a pulsed molecular beam valve, which admitted pulses of the precursor of about 1 msec. duration; a differentially pumped quadrupole mass spectrometer, and an Auger spectrometer, both mounted at a 90° angle to the pulse valve source. The system also was provided with a second mass spectrometer, in line of sight to the pulse valve, and an ion gun, used to clean the sample surface by argon ion etching. The conditions necessary for precursor decomposition, on the glassy carbon surface, and the gas-phase decomposition product flux were obtained by setting various substrate temperatures, then recording the magnitude of the scattered signal for each of the m/e that showed a pulsed waveform.

RESULTS AND DISCUSSION

The main features of the mass spectrum of the cyclic carbosilane precursor I, along with a set of structural assignments for the various fragments evidenced in this mass spectrum, is given in Table I.

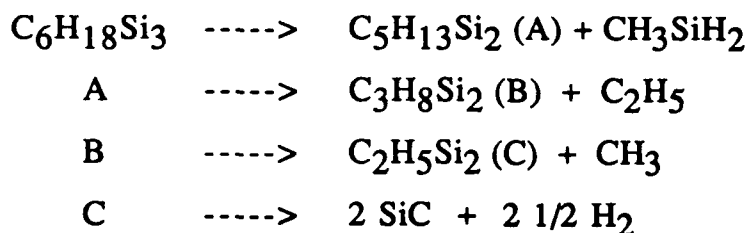
Our initial thermal desorption studies on a silicon surface using the $m/e = 73$ peak of the precursor as a measure of the intact precursor molecule indicated two desorption peaks of approximately equal intensity at ca. 150 and 185 $^\circ\text{K}$, suggesting the existence of two

distinct surface adsorbed species with slightly different adsorption energies [6]. As is clear from Figure 1, this precursor can exist in two isomeric forms which differ by the relative position of the two Me groups on the ring Si atoms (cis and trans). In that our NMR spectral studies of the compound obtained from the preparative procedure employed show two sets of peaks in approximately equal intensities corresponding to each of the chemically distinct atoms in this structure, we tentatively associate the two thermal desorption peaks with the cis- and trans- isomers of I, which are apparently produced in equal amounts by this procedure.

On a glassy carbon surface, both forms of this precursor apparently adsorb much more strongly than on Si, as no desorption is seen until ca. 50 °C. The behavior of the peak at $m/e = 159$, taken as a measure of scattered, unreacted precursor, is shown in Figure 2. The low value of the observed signal at temperatures below 200 °C is due to demodulation of the pulsed signal by the relatively long surface lifetime in the physically adsorbed state. All of the other fragment peaks distinguishable at low temperature showed the same behavior as $m/e = 159$, with the exception of $m/e = 45$. In addition, as the temperature was increased, product peaks were observed at $m/e = 15$ and 29. The temperature dependence of these peaks is shown in Figure 3, where the $m/e = 45$ intensity has been corrected for the contribution arising from fragmentation of the parent molecule in the ion source.. These data suggest an onset for reaction on the carbon surface of ca. 400 °C. Essentially identical results obtained in repeat runs on the same surface indicate that these

observations relating to decomposition of the precursor on carbon are also relevant to the growth of the SiC film.

Based on the foregoing findings, the reaction scheme shown below is suggested.



In this reaction scheme the three species evolved are tentatively identified as the methylsilyl radical, CH_3SiH_2 , along with the methyl and ethyl radicals. The species labeled as "A", "B" and "C" in this scheme are presumed to be adsorbed on the surface while the CVD process is taking place and no information regarding their nature is currently available; however, based on previous studies of organosilane decomposition reactions and the supposition that there is a significant amount of strain energy stored in the cyclic four-membered $(\text{SiC})_2$ ring, we anticipate that these species are ring-opened radicals which have reacted with the surface, effectively anchoring the remaining Si atoms to the surface. The observation of close-to-stoichiometric SiC as an end product of this deposition, species of $m/e = 29$ and 15 as major products of this high vacuum thermal decomposition study, and methane, ethylene, acetylene, and ethane among the isolated volatile products of the CVD experiment [4], suggest that the excess carbon which is initially present in this in the precursor is efficiently lost to the gas phase, presumably as

CH_{4-x} ($x = 0$ or 1) and C_2H_{6-x} ($x = 0 - 4$). Clearly, further studies are needed in order to definitively characterize the reactions occurring on the substrate surface during CVD of the precursor I; however, it is clear that, at the present stage of our understanding of low temperature CVD of SiC using carbosilanes, any direct associations between the structure and stoichiometry of the precursor and the temperature at which decomposition will take place or the film composition are open to question.

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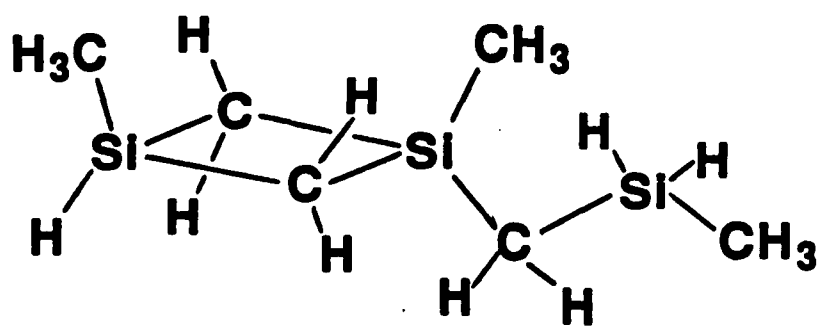
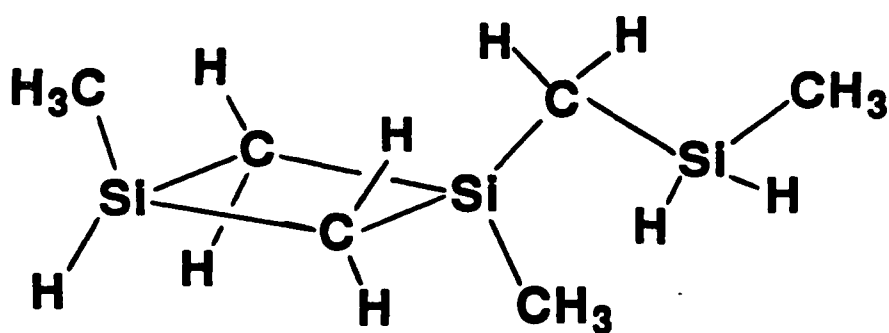


Figure 1

